Effective radii of noble gas atoms in silicates from first-principles molecular simulation

LIQUN ZHANG,1,2 JAMES A. VAN ORMAN,1,* AND DANIEL J. LACKS2

1Department of Geological Sciences, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.
2Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

ABSTRACT

An understanding of how noble gas atoms are dissolved in mantle minerals and melts is necessary to infer geological information from the constraints provided by noble gas geochemistry. For this purpose, first-principles molecular simulations are carried out on liquid and crystalline (stishovite) silica systems with dissolved noble gas atoms (He, Ne, Ar, Kr, and Xe). The first principles nature of the simulations, which do not involve empirical force field parameters, enables the determination of the effective radii and structural environments of the noble gas atoms. The noble gas atoms are shown to be highly compressible, so that their effective radii depend strongly on the molar volume of the system (which in turn depends on pressure). Due to the continuous nature of interatomic forces, the effective radii also depend on the extent to which the surrounding atoms can relax in response to the presence of the noble gas atom. In this regard, different definitions of effective radii are relevant in different situations: “equilibrium radii” that correspond to the optimal interatomic distances at the molar volume of the system, and “repulsive wall” radii that correspond to the interatomic distances where the interatomic potentials of mean force change from attractive to repulsive at that molar volume. The equilibrium radii determine the interatomic distances in a melt, and the repulsive wall radii determine the interatomic distances for interstitial sites in a crystal. Based on these effective radii, the structural environment surrounding the noble gas atoms at high pressure is shown to correspond to a close packing of O atoms around the central noble gas atom. Compression of the noble gas atoms is shown to correspond closely to the compression of the porosity within the silicate melt structure.

Keywords: Silicate melt, ionic radius, molecular dynamics simulation, density functional theory

INTRODUCTION

The noble gases and their isotopes are important tracers in mantle geochemistry, providing unique insight into the structure of the deep Earth, its formation and differentiation, and the style and efficiency of mantle convection (e.g., Allègre et al. 1987, 1996; Ozima and Igarashi 2000; Parman 2007). Noble gases are commonly considered to behave as perfectly incompatible elements during partial melting in Earth’s upper mantle, entering the melt en masse as soon as melt forms, then degassing to the atmosphere during ascent and eruption. Melting is thus often approximated as a perfectly efficient process for removing noble gases from the mantle, with noble gases completely extracted from regions of the mantle that have undergone partial melting.

This simple picture of noble gas behavior during mantle melting is increasingly difficult to reconcile with experimental data on the solubility of noble gases in mantle minerals, and on their partitioning between minerals and melts. The experimental data themselves vary over a wide range among different studies and have profoundly different implications for the extraction of noble gases from the mantle. Some recent studies (e.g., Brooker et al. 2003; Heber et al. 2007) have found that noble gases are indeed highly incompatible in mantle minerals, but still have sufficient solubility to be partially retained in the mantle during partial melting. In another recent study, Parman et al. (2005) found that He is less incompatible than U and Th during mantle melting and that, contrary to the usual interpretation, high 3He/4He ratios in basalts may be derived from depleted rather than enriched mantle sources. Other recent experimental studies on the solubility of argon in mantle minerals (Watson et al. 2007; Thomas et al. 2008) indicate that it behaves as a compatible element during mantle melting, with a solid/melt partition coefficient >>1. These results imply that Ar would be retained in the mantle despite extensive partial melting, and that other mechanisms may be necessary to explain the accumulation of 40Ar in Earth’s atmosphere.

The change with pressure in the solubility of noble gases in silicate melts is also incompletely understood. It is well established that the solubility of noble gases increases with pressure up to ~5 GPa (White et al. 1989; Montana et al. 1993; Chamorro-Pérez et al. 1996, 1998; Schmidt and Keppler 2002; Bouhifd and Jephcoat 2006). At higher pressures the noble gas solubility may plateau (Schmidt and Keppler 2002; Chamorro-Perez et al. 1996) and/or may drop abruptly at pressures between 5 and 18 GPa (Chamorro-Pérez et al. 1996, 1998; Bouhifd and Jephcoat 2006). The discontinuous drop in solubility at high pressures is not well understood from a mechanical perspective. Sarda and Guillot (2005) were able to reproduce the observed variation in Ar solubility with pressure up to ~5 GPa, in a range of melts, using an empirical hard sphere model for the melt. Their model

* E-mail: james.vanorman@case.edu
was unable to explain a precipitous decline in solubility with pressure, and these authors suggested that an abrupt change in the melt structure, not described by the hard sphere model, may be necessary to explain such behavior.

It is clear that to interpret accurately the constraints provided by noble gas geochemistry, it is necessary to have a better understanding of how noble gas atoms are dissolved in mantle minerals and melts. The sites that noble gas atoms occupy in minerals are very poorly known, and there is a lack of reliable information on basic properties of the noble gas atoms themselves, especially their radii and how they change with pressure and the local structural environment. The solubility of an element in a mineral is a strong function of the radius of the atom or ion relative to the ideal radius of the crystallographic site it occupies. Blundy and Wood (1994) presented a model that quantifies this dependence, and the model has been widely applied to the partitioning of trace elements between minerals and silicate melts, including the noble gases (Wood and Blundy 2001; Brooker et al. 2003). The solubility of noble gases in melts is also considered to depend primarily on the sizes of the atoms and on the availability of spaces in the melt structure large enough to accommodate them (Lux 1987; Carroll and Stolper 1993; Guillot and Guissani 1996; Sarda and Guillot 2005). While the radii of most trace elements are well known based on crystallographic data (Shannon 1976), the radii of neutral noble gas atoms are much less well established. To our knowledge there exists only one experimental measurement of the radius of a noble gas atom dissolved in a condensed phase, based on EXAFS data for Kr dissolved in vitreous silica (Wulf et al. 1999). Zhang and Xu (1995) provided estimates of neutral noble gas radii by interpolating (or extrapolating) to zero charge the charge vs. radius data for cations and anions with identical electronic structures. The basis for these estimates is reasonable, but data on the radii of noble gas atoms, and on their unknown dependences on pressure and local structural environment, are needed.

Here, we present noble gas radii based on ab initio molecular dynamics simulations of noble gases dissolved in liquid and crystalline silica (SiO$_2$). Previous molecular simulations of noble gases dissolved in silicate melts and minerals (Guillot and Guissani 1996; Du et al. 2008) have relied on empirical interatomic potentials. These simulations provide essential insights, but are limited by the sparse data available to calibrate interatomic potentials involving noble gas atoms. This limitation makes them unsuitable, in particular, for determining the radii of noble gas atoms (i.e., the radii of the noble gas atoms are in essence empirical inputs to the simulation, not results of the simulation). Our simulations avoid this issue by utilizing non-empirical potentials based on density functional theory. The methods have been well established to provide accurate results for a wide range of materials, but have not been applied previously to noble gases dissolved in condensed phases. Based on the results, we derive atomic radii for He, Ne, Ar, Kr, and Xe and evaluate their changes with pressure and local structural environment. The noble gases dissolved in liquid silica are found to be far more compressible than silicon and oxygen, and cannot be considered to have fixed radii under mantle conditions. The effective size of a noble gas atom depends significantly on pressure, and also on the type of site it occupies.

**Simulation Details**

First-principles molecular dynamics (FPMD) simulations are used to study the structures of liquid silica systems with dissolved noble gas atoms. The simulations are carried out with the VASP computer program (Kresse and Furthmüller 1996a, 1996b, 2008; Kresse and Hafner 1993, 1994a). In these simulations, the classical dynamics of the nuclei are determined, based on forces obtained with a density functional theory solution of the electronic structure. We emphasize that the density functional calculations of the interatomic forces are not exact, due to the limited basis set, the use of approximate pseudopotentials to represent the core electrons, and the approximate nature of the density functional.

To connect our results with the recent FPMD results for pure silica liquids of Karki et al. (2007), the same methodology for the electronic structure calculation is used. In particular, the local density approximation (LDA) functional (Perdew and Zunger 1981) is used with a plane wave cutoff of 400 eV and gamma point sampling, and ultra-soft pseudopotentials (Vanderbilt 1990; Kresse and Hafner 1994b) are used where available. While these pseudopotentials are available for Si, O, Ne, Kr, and Xe, they are not available for He and Ar, and so the projector-augmented wave pseudopotentials (Kresse and Joubert 1999; Blöchl 1994) are used for these atoms; tests on Ne with the two types of pseudopotentials showed that the results are insensitive to the type of pseudopotential used.

The simulations are performed in the canonical ensemble, such that the number of atoms in the system, the temperature (T), and the volume (V) are kept constant. The systems studied include 32 Si atoms, 64 O atoms, and one noble gas atom; these compositions correspond to mass percentages of the noble gas species ranging from 0.2% for He to 6% for Xe. A time step of 1 fs is used in the simulation, and the results reported here are based on simulations with durations of 24–28 ps. Most simulations are carried out at $T = 4000$ K, which is near the lowest temperature for which the systems reliably equilibrate in the duration of the simulation. The simulations are carried out in cubic simulation cells, with periodic boundary conditions used to remove surface effects. The volumes range from $V = 27.57$ to 13.79 cm$^3$/mol; the FPMD results of Karki et al. (2007) show that this volume range corresponds to pressures ranging from 0 to 50 GPa (note that the pressures in the present systems will be slightly higher due to the addition of the rare gas atom to the same volume).

**Results**

**Radial distribution functions**

The local structure in liquid systems can be characterized by the radial distribution function, $g(r)$, which represents the relative probability of finding an atom at the distance $r$ from a given atom. The values of $g(r)$ go to zero at small $r$ due to the steric repulsion between atoms, and the values of $g(r)$ go to 1 for large $r$ (in disordered systems) indicating the absence of correlation in the positions of atoms at large $r$. Peaks and valleys in $g(r)$ indicate increased and decreased probabilities of finding atoms at that distance $r$.

The local environment surrounding a noble gas atom in liquid silica can be understood by comparing the radial distribution
functions for the interactions X-Si and X-O, where X represents a noble gas atom. Figure 1 shows these radial distribution functions for X = Ar. Note that the initial increase of g(r) occurs at smaller r for O than for Si, which indicates that the Ar atom has O atoms as its nearest neighbors. This result is generally valid for the other rare gas atoms as well, and is in agreement with the results of previous molecular dynamics simulations based on empirical interatomic forces (Angell et al. 1988; Guillot and Guissani 1996).

The dependence of the X-O radial distribution functions on the type of noble gas atom is shown in Figure 2. As the atomic number of the noble gas atom increases, the initial increase of g(r) shifts to larger r; i.e., the steric repulsion of the atom increases as its atomic number increases because of the larger number of electrons.

The radial distribution functions change significantly with changing volume. As an example, the effects of volume on the g(r) results for Ar-O are shown in Figure 3. As the volume decreases, the radial distribution function develops a much more pronounced first peak and valley, both of which move to smaller values of r. This result indicates that with decreasing volume the O atoms surround the argon atom more closely and in a more ordered way.

Coordination number

The coordination number is the number of nearest neighbor atoms that surround a central atom. The nearest neighbors are represented by the first peak of the radial distribution function, the upper limit of which is usually defined to be the position of the first valley. The coordination number can be obtained by integrating the area under the first peak of the g(r); i.e., integrating g(r) from 0 to the position of the first valley. We determined the coordination numbers for the silicon and noble gas atoms in this way, using the radial distribution functions for Si-O and X-O, respectively.

Numerical noise obscures the precise positions of the first valley in the g(r). To unambiguously estimate these positions, the g(r) results are fitted to a sixth-order polynomial, from which the positions can be determined. Since the polynomial would not fit well the sharp increase of g(r) at small r, the fitting is carried out only for values of g(r) > 0.8. The uncertainty in determining these positions is approximately 0.05 Å at larger volumes, and 0.01 Å at smaller volumes [this uncertainty is estimated by the variability in the results obtained by fitting to different ranges of g(r)].

The coordination numbers for the silicon and noble gas atoms are shown in Figure 4. For silicon, the results are similar to those of previous studies on the pure liquid silica system (Karki et al. 2007), indicating that the presence of the noble gas atom has little effect on silicon coordination. For decreases in volume <20%,
the silicon coordination number remains essentially constant at 4, but for greater decreases in volume the coordination number increases toward a value of 6.

The coordination of the rare gas atoms exhibits very different behavior. First, these coordination numbers range from 5 to 17, and are thus usually much larger than those for silicon; a snapshot of the local environment of a noble gas atom (Xe), which shows this large coordination, is shown in Figure 5. Second, for decreases in volume <20%, the coordination number increases with decreasing volume, but for greater decreases in volume the coordination number remains essentially constant; this volume dependence is opposite to that found for silicon.

Thus there are two distinct regimes of compression. In the first regime (volume decreases <20%), the coordination number of the silicon remains constant but the coordination number of the noble gas atom increases. In the second regime (volume decreases >20%), the coordination number of silicon increases toward a value of 6.

Effective radii of noble gas atoms

Any definition of the radius of an atom is essentially arbitrary, since the electron distributions that are the physical basis of any

**Figure 4.** Coordination numbers in liquid silica at $T=4000$ K, for (a) noble gas atoms; (b) Si atoms. Results are for liquid silica systems with one atom of: He (circles), Ne (squares), Ar (diamonds), Kr (up-pointing triangles), or Xe (left-pointing triangles). Uncertainties were estimated by calculating the average value of CN for separate time segments, each ~4 ps in duration. The error bars show ±2 standard deviations of these average values.

“atomic size” are continuous. In this paper, we define two types of effective atomic radii in terms of the potential of mean force. The potential of mean force $w(r)$, which is related to the radial distribution function by $w(r) = -kT \ln g(r)$ (Chandler 1987), represents an effective interatomic potential that accounts for the effects of all other atoms in the system. The two types of effective radii we define are an “equilibrium radius” $R_e$ that corresponds to the optimal atomic separations, and a “repulsive wall” radius $\sigma$ that corresponds to the distance at which the potential of mean force becomes repulsive. The relationships of these two types of radii to the potential of mean force are shown in Figure 6. These two types of radii convey different information: $R_e$ is related to the interatomic distance in situations where the noble gas atom environment is fully relaxed (e.g., in a melt), and $\sigma$ is related to the interatomic distance in situations where the noble gas atom environment is highly constrained (e.g., in an interstitial site of a crystal). Again, we stress that these effective radii are parameters that partially characterize the spatially continuous atomic interactions; they serve as approximate, rather than rigorous, predictors of interatomic distances (rigorous predictions require detailed simulations such as carried out here).

The value of $R_e$ is based on the position of the first peak of the radial distribution function for atoms that are nearest neighbors; the position of this peak represents the most probable distance of separation, and so this definition is such that the sum of the $R_e$ of two atoms is their most probable nearest neighbor separation. The $R_e$ of an O atom is obtained as half the distance of the first peak of the O-O radial distribution function (note that O atoms in silica are much larger than Si atoms, and so O atoms are nearest neighbors in silica). The $R_e$ of the noble gas atom is obtained as the distance of the first peak of the X-O radial distribution function minus the value of $R_e$ for the O atom.

The value of $\sigma$ is based on the position in which the radial distribution function passes through the value of 1; since the potential of mean force $w(r)$ is related to the radial distribution function by $w(r) = -kT \ln g(r)$ (Chandler 1987), this definition is such that the sum of the $\sigma$ of two atoms is the separation at

**Figure 5.** Snapshot of the local environment of a Xe atom in liquid silica at 4000 K and $V=13.79$ cm$^3$/mol, obtained using the VMD program (Humphrey et al. 1996, 2008). The Xe atom is at the center, and the surrounding spheres are O atoms. The 16 O atoms are within the distance of the first valley of the radial distribution function.
which the potential of mean force becomes repulsive. These values are obtained from the O-O and X-O radial distribution functions in a way analogous to the method for obtaining $R_e$, as described above.

The results for the effective radii of the noble gas atoms in silica are shown in Figure 7. Note that values of $R_e$ for He and $\sigma$ for He and Ne at $V = 27.57$ cm$^3$/mol are not reported because numerical noise coupled with relatively flat $g(r)$ curves render their values unreliable. The effective radii decrease with decreasing volume (as also evident in Fig. 3). The oxygen radii also decrease, but over a much smaller range (e.g., the radii for oxygen range are $R_e = 1.31$ Å and $\sigma = 1.14$ Å at $V = 27.57$ cm$^3$/mol, and $R_e = 1.19$ Å and $\sigma = 1.04$ Å at $V = 13.79$ cm$^3$/mol). The results for the noble gas radii as a function of volume are correlated with the following equations:

$$R_e(V) = R_{e,0} + R_e' (V/V_0 - 1)$$  \hspace{1cm} (1)

$$\sigma(V) = \sigma_0 + \sigma' (V/V_0 - 1)$$  \hspace{1cm} (2)

where $R_{e,0}$ and $\sigma_0$ are the effective noble gas radii at $V = V_0 = 27.57$ cm$^3$/mol [$V_0$ is the volume at ambient pressure (Karki et al. 2007)], while $R_e'$ and $\sigma'$ are parameters describing how the effective noble gas radii change with volume. The simulation results are fitted to Equations 1 and 2, and the fitted values for $R_{e,0}$, $\sigma_0$, $R_e'$, and $\sigma'$ are given in Table 1.

**Results for a noble gas atom in stishovite**

The relevance of the melt results to crystalline systems is examined by carrying out simulations of noble gas atoms in interstitial sites of stishovite, which is the stable crystal phase of silica at high pressure. Stishovite was chosen for two reasons. First, since stishovite is a very dense phase, it provides a stringent test for ideas concerning the incorporation of interstitial atoms. Second, the high symmetry of the stishovite structure allows a straightforward analysis of the deformation of the crystal resulting from the incorporation of the noble gas atom.

Simulations are carried out with the silicon and O atoms initially in the appropriate crystallographic positions for stishovite, i.e., space group $P4_2/mnm$, (Baur and Kahn 1971), and the simulation cell dimensions appropriate for stishovite at ambient conditions ($V = 14.05$ cm$^3$/mol); these systems correspond to $2 \times 2 \times 4$ unit cells of stishovite.

The single noble gas atom is inserted into the largest interstitial site (Wyckoff special position $c$) in the structure. This interstitial site has two neighboring O atoms at a distance of 1.51 Å, and two neighboring Si atoms at a distance of 2.09 Å; all other atoms are at distances $>2.8$ Å. Thus, the insertion of the noble gas atom will cause local distortion of the stishovite structure, which is of course dependent on the type of noble gas atom. Energy minimizations are carried out to determine the structures that minimize the energy of the system (note that these are not molecular dynamics simulations, as were carried

<table>
<thead>
<tr>
<th>Noble gas</th>
<th>$R_{e,0}$ (Å)</th>
<th>$R_e'$ (Å)</th>
<th>$\sigma_0$ (Å)</th>
<th>$\sigma'$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.32</td>
<td>1.12</td>
<td>1.14</td>
<td>1.02</td>
</tr>
<tr>
<td>Ne</td>
<td>1.50</td>
<td>1.00</td>
<td>1.27</td>
<td>0.82</td>
</tr>
<tr>
<td>Ar</td>
<td>1.95</td>
<td>1.42</td>
<td>1.73</td>
<td>1.33</td>
</tr>
<tr>
<td>Kr</td>
<td>2.00</td>
<td>1.28</td>
<td>1.82</td>
<td>1.23</td>
</tr>
<tr>
<td>Xe</td>
<td>2.22</td>
<td>1.49</td>
<td>2.04</td>
<td>1.52</td>
</tr>
</tbody>
</table>
The results for the smallest X-O distances are shown in Figure 8. For all noble gas atoms, there is some local distortion of the crystal lattice in the neighborhood of the occupied interstitial site—i.e., the X-O distance is greater than the value 1.51 Å that would occur in the absence of the noble gas atom. As expected, the magnitude of the lattice distortion increases as the atomic number of the noble gas atom increases. In all cases, the integrity of the crystal structure is maintained, and the lattice distortions are relatively minor, localized, and preserve the symmetry.

Figure 8 shows that these smallest X-O distances in stishovite are almost exactly equal to the sum of the repulsive wall radii for the noble gas atom and oxygen obtained from the simulations on liquid silica. Recall that the “repulsive wall” radius $\sigma$ corresponds to the distance at which the interatomic potential becomes repulsive; therefore, there is a large energy penalty for X-O distances $< (\sigma_X + \sigma_O)$. The results in Figure 8 demonstrate that $\sigma$ indeed determines the interatomic distance in situations where the noble gas atom environment is highly constrained (e.g., in an interstitial site of a crystal). We note that the near-exact agreement between the smallest X-O distances and $\sigma_X + \sigma_O$ is fortuitous—as pointed out above, the values of $\sigma$ are measures of the distance where repulsive interactions begin to dominate, but since the interatomic potentials are continuous the onset of interatomic repulsion occurs gradually over a range of distances.

As evident in Figure 8, for the smaller atoms the smallest X-O distances are greater than $\sigma_X + \sigma_O$, while for the larger atoms the opposite is true. This result is understandable because the local distortion of the lattice surrounding the rare gas atom, which is required in order for the smallest X-O distances to become comparable to $\sigma_X + \sigma_O$, introduces a lattice energy penalty that increases strongly with the magnitude of the lattice distortion. This energy penalty, which acts to reduce the lattice distortions, is more significant for the larger noble gas atoms because these atoms require larger lattice distortions.

**Discussion**

**Comparison with experiment**

We are aware of one experimental investigation of the structural environment of noble gas atoms in liquid silicate systems (Wulf et al. 1999). In this study, Kr was dissolved in a supercooled silica melt at 1473 K and 0.7 GPa; after allowing the system to equilibrate, the supercooled liquid was quenched to form a glass, and X-ray absorption experiments were used to address the structural environment of Kr in the glass. From these experiments, the average Kr-O nearest neighbor separation was determined to be 3.45 ± 0.1 Å.

To compare with this experimental result, the average Kr-O nearest neighbor separation is determined from the present simulation results [note that the average separation differs in general from the position of the peak of $g(r)$, and is obtained by integration of $g(r)$ from $r = 0$ up to the distance of the first valley of $g(r)$]. The present result for the average Kr-O nearest neighbor separation is 3.50 Å, which is in good agreement with the experimental result.

**Coordination numbers of the noble gas atoms**

The coordination number results for the noble gas atoms can be understood in terms of the packing of “hard” (impenetrable) spheres. More specifically, we address the following question: if the noble gas atom is modeled as a hard sphere of radius $R_1$, and the O atoms are modeled as hard spheres of radius $R_2$, what is the largest number of O atoms that can be in contact with the noble gas atom? The problem of the maximum number of hard spheres of radius $R_1$ that can pack around a hard sphere of radius $R_2$ has been solved (Clare and Kepert 1986; Kottwitz 1991). Note that this problem is equivalent to the problem of how many two-dimensional circles of radius $R_2$ can pack on the surface of a sphere of radius $R_1 + R_2$. The solutions to this problem are shown as the solid line in Figure 9 as a function of the ratio of the diameter of the circles relative to the radius of the sphere.

This theoretical picture is used to address the packing of O atoms around the noble gas atom. The diameter of the two-dimensional circle ($D_{\text{circle}}$) corresponds to the diameter of the O atom, obtained as the distance of the first peak of the O-O radial distribution function. The radius of the central sphere ($R_{\text{sphere}}$) corresponds to the sum of the radii of the noble gas atom and the O atom, obtained as the distance of the first peak of the X-O radial distribution function. Figure 9 shows the coordination number results obtained in the simulations (as described in the Results section) as a function of the ratio $D_{\text{circle}}/R_{\text{sphere}}$, where $D_{\text{circle}}$ and $R_{\text{sphere}}$ are obtained as described in this paragraph.

Figure 9 shows that, at smaller volumes (volume decreases greater than 20%), the simulation results are very similar to the hard-sphere closest-packing results; i.e., the packing of O atoms around the noble gas atom is well described as closest packing. In contrast, at larger volumes (volume decreases < 20%) this is not the case; there are fewer O atoms surrounding the noble gas atom than expected in the case of close packing.

The approach toward closest packing can explain the origin...
of the two regimes of compression evident in Figure 4. Compression of the system at larger volumes causes more O atoms to be “pushed” near the noble gas atom; in this regime the coordination number increases with compression. After sufficient compression there is no more available space around the noble gas atom because O atoms have become close packed around the noble gas atom; in this regime the coordination number remains constant as the system is compressed.

Comparison with previous estimates of rare gas atom size

Our results for the effective radii of the noble gas atoms in liquid silica at 4000 K, and a volume corresponding to ambient pressure, are shown in Table 1. Zhang and Xu estimated radii of the noble gas atoms dissolved in other materials from interpolation or extrapolation of the radius-charge relations for isoelectronic ions in crystals (Zhang and Xu 1995). Their estimated radii are significantly smaller than the values of \( R_e \) found here, being on average 17\% smaller (note that their radii are based on the equilibrium bond distances of crystals, and are thus analogous to our “equilibrium radii,” \( R_e \), rather than our “repulsive wall” radii, \( \sigma \)). A factor that leads to this discrepancy is that the crystal structures used to derive these effective radii are composed of ions with coordination numbers ranging from 4 to 8; however, the coordination numbers of the noble gas atoms in liquids are (in almost all cases) significantly larger.

Guillot and Guissani (1996) determined X-O radial distributions in silica using molecular dynamics simulations with empirical interatomic potentials. The distances they obtain for the first peaks of the X-O radial distribution function, at 4000 K and a density 2.2 g/cm\(^3\), are significantly larger than found here: 10\% larger for He, and 25\% larger for Ar. The first principles methodology used here for the interatomic forces is expected to make the present results more reliable.

The ambient pressure values of \( R_e \) determined here are very close to the spherical noble gas radii determined from the lattice parameters for fcc Ne, Ar, Kr, and Xe crystals at 4–58 K (Wyckoff 1963). In each case the agreement is better than 5\%, and the noble gas crystal radii are not systematically larger or smaller than the equilibrium radii determined here. However, at higher pressures (Jephcoat 1998; Dewaele et al. 2008) the radii of noble gases in the pure fcc crystals are systematically larger than the equilibrium radii determined here. The noble gas crystal radii are ~10\% larger for Ar, Kr, and Xe at 50 GPa (corresponding to \( V/V_0 \approx 0.5 \) in the present study). At first glance this seems surprising, because the noble gas radii scale so well with volume, and the noble crystals are more compressible than liquid silica (Jephcoat 1998; Karki et al. 2007). However, in contrast to the noble gas crystals, compression of liquid silica is accomplished by a collapse of the melt structure, with very little compression of the Si and O atoms themselves. Because the noble gases occupy spaces in the melt framework rather than Si or O sites, it is the compressibility of the “free space” within the melt structure, or “ionic porosity” (Carroll and Stolper 1993), that is expected to be relevant. This “free space” in the liquid silica (i.e., the volume that is not occupied by Si and O atoms) is more compressible than any of the noble gas crystals, and closely matches the volume compression of the noble gas atoms dissolved in liquid silica (Fig. 10).

Comments on the variation in noble gas solubility with pressure

There have been several reports of a sharp decrease in noble gas solubility with pressure in silicate melts (Chamorro-Pérez et al. 1996, 1998; Bouhifd and Jephcoat 2006). In liquid silica, the data for Ar show a continuous increase in solubility up to 5 GPa, then a sharp decrease in the solubility, one order of magnitude over the pressure interval from 5 to 6 GPa (Chamorro-Pérez et al. 1996). There is some controversy over whether this drop in solubility is real. The results of Schmidt and Keppler (2002) for a fully polymerized haplogranitic melt are consistent with those of Chamorro-Pérez et al. (1996) up to 5 GPa, but beyond this pressure the solubility remains approximately constant up to at least 8 GPa. Bouhifd and Jephcoat (2006) suggested that the Al content of the melt controls the pressure at which the drop in solubility occurs, and that this may explain the apparent discrepancy in the results for polymerized melts. Sarda and Guillot (2005) modeled the solubility of noble gases, using a simple hard sphere model for the noble gas and for the silicate melt. The results were found to provide a good description for the solubility as a function of pressure for a range of silicate melts at relatively low pressures, including a plateau in the solubility in the ~5–10 GPa range, but could not explain a sharp drop in solubility with pressure. Sarda and Guillot (2005) suggested that such a change might be accounted for by an abrupt change in the melt structure that was not accounted for in the hard sphere model.

The solubility of noble gases in silicate melts is strongly correlated with the size of the noble gas atom and the openness of the melt structure, in particular the ionic porosity (Carroll and Stolper 1993). The radii of the noble gases vary linearly with the molar volume of the melt (Fig. 7), and with the ionic porosity,
calculated as \((1 - V_{ca}/V_m)\), where \(V_{ca}\) is the volume occupied by silicon and O atoms, and \(V_m\) is the melt volume (Fig. 10). These parameters vary continuously, rather than abruptly, with melt volume (and thus with pressure). As discussed above, the local environment surrounding the noble gas atom evolves to a more densely packed structure as the melt volume decreases, with closest packing achieved after ~20% compression. This corresponds to a pressure of ~5 GPa (Karki et al. 2007), which, as mentioned above, is the pressure at which the abrupt decrease of Ar solubility in liquid silica has been reported. It is possible that the decrease in Ar solubility in silica is related to this transition to closest packing; Nevins and Spera (1998) made the similar suggestion that the drop in Ar solubility in molten anorthite was related to a collapse of the silicate ring structure at high pressure. However, it remains unclear whether such gradual structural transformations can account for abrupt changes in noble gas solubility.

**CONCLUDING REMARKS**

First-principles molecular simulations have been used to determine the effective radii of noble gas atoms in silica. Direct experimental results on this and related properties are sparse, but the simulation results are in good agreement with an experiment for Kr in silica (Wulf et al. 1999). The noble gas atoms are highly compressible, and so defining a single radius to describe the size of a noble gas atom is not appropriate. Rather, the effective radius depends on the volume of the system (which in turn depends on pressure), and on the extent to which the surrounding atoms can relax in response to the presence of the noble gas atom.

In regard to the volume dependence, the effective radii of the noble gas atoms decrease by 30–40% for volumes corresponding to the pressure increase of 0 to 50 GPa (for the relationship between volume and pressure see Karki et al. 2007); in comparison, the effective radii of the O atoms decrease by <10% in this pressure range. The much higher compressibility of the noble gas atoms in comparison to the other components in silicates means that more care needs to be taken in choosing the radii that are relevant to the particular problem being considered. Different definitions of the effective radii are necessary depending on the extent to which the surrounding atoms can relax in response to the presence of a noble gas atom. In a melt, the atoms can move to accommodate the noble gas atom to the same extent that they accommodate all other atoms in the melt, and so the radius of the noble gas atom is determined by the distance for the most favorable interactions with its neighbors, and the radius of interest is the equilibrium radius given in Table 1. In contrast, the long-range lattice structure of a crystal tethers the atoms to lattice sites, with energy penalties for displacements from these sites. As a result, the radius of a noble gas atom in a highly constrained lattice site is determined by the distance where the interaction with its neighbors becomes repulsive. The repulsive radii given in Table 1, or the radii estimated by Zhang and Xu (1995) for neutral noble gas atoms in particular coordination environments, are more relevant to the solubility of noble gas atoms in minerals, and to the prediction of mineral/melt partition coefficients.

**ACKNOWLEDGMENTS**

This material is based upon work supported by the National Science Foundation under grant number EAR-0635820, and a grant of computing time from the Ohio Supercomputer Center. The constructive comments of Frank Spera and an anonymous reviewer helped improve the manuscript.

**REFERENCES CITED**


**FIGURE 10.** Compression of noble gas atoms vs. compression of the free space in liquid silica. The cube of the equilibrium radii, relative to the radii at ambient pressure, are plotted against the “free” volume of the melt (i.e., the volume unoccupied by silicon and O atoms) relative to the free volume at ambient pressure. Symbols are plotted as: He (circles), Ne (squares), Ar (diamonds), Kr (up-pointing triangles), and Xe (left-pointing triangles).


